# *Thermodynamics Resource*: A Database for Industrial High-Temperature Applications


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**Industrial Technologies Program**
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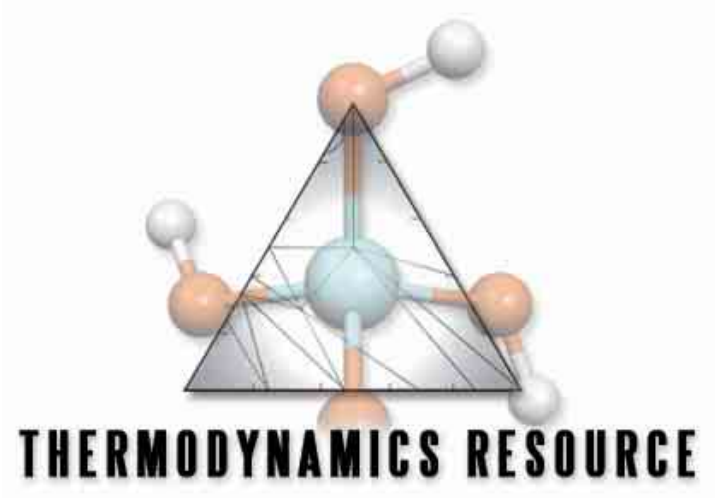
**Project review meeting**
**Washington, D. C.**
**June 22 – 23, 2004**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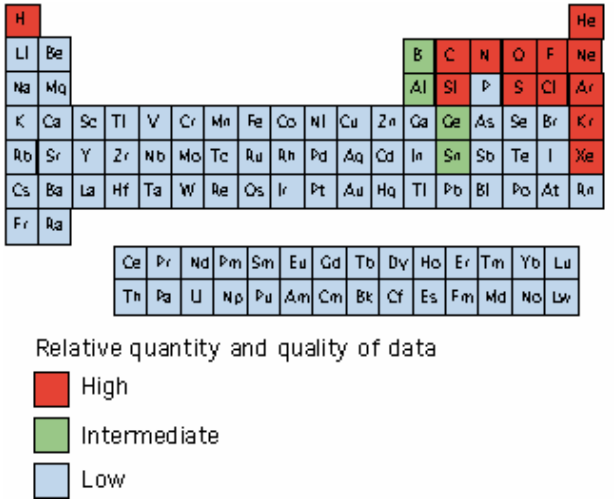
# Thermochemical data are essential for the design, optimization, and control of high-temperature processes

**Goal:** Provide thermochemical data and models for an important set of industrial materials: refractories, glasses, and metals

**Challenge:** Decline in research efforts over past 20 years has lead to huge gaps in the database without substantial experimental efforts. New theoretical methods and models must be developed to provide the data




**Benefits:**

- Quantitative models of industrial processes
- Thermodynamic efficiency/heat balances
- Selection of materials of construction based on real understanding of their stability
- Reduce emissions by optimizing combustion

- **FY05 Activities:** Expand gas-phase dataset for Ti, Cr, Mn, Fe. Develop methods for Y, Zr, Nb, Mo. Expand condensed-phase dataset for K, Mg, Cr, Ti, P oxides, and generate increasingly large global models.

**Participants:** Sandia National Laboratories, Oak Ridge National Laboratory, NASA Glenn Research Ctr.

# Barrier-Pathway Approach

## *Barriers*

- Very limited data for refractories, glasses, and high-T gas-phase species
- Experimental data for model verification absent
- No consistent, documented, continuously updated, and fully open repository for data

## *Pathways*

- Create models and develop theory needed to predict thermochemistry from first principles
- Team with NASA/Glenn to provide critical experimental data
- Create user-friendly web site

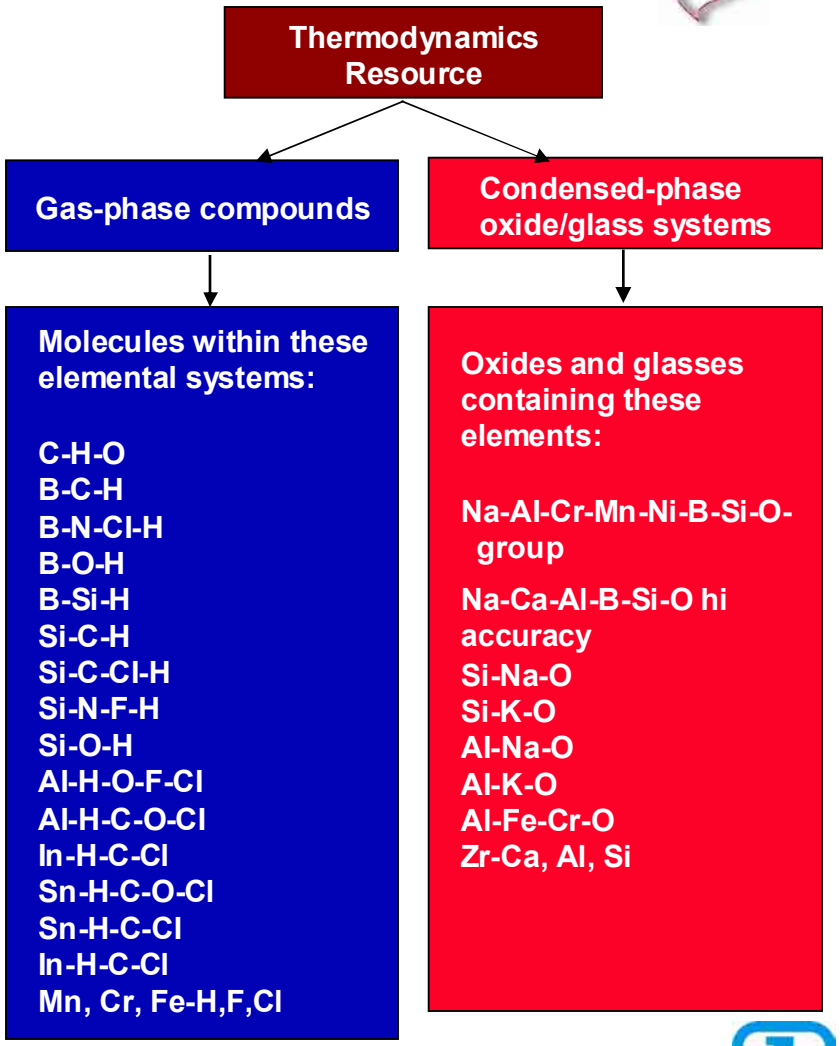
## *Critical Metrics*

- Generate data for all major refractory/glass systems
- Predicted data agree with experiment (where avail.)
- Web site receives high level of hits and on-line subscribers
- Direct application projects, including G+, M+

| Benefits (est.) | 2020 |
|---|---|
| Energy Savings (trillion BTU) | 30 |
| Cost Savings ($Million/y) | 145 |
| Carbon Reduction (1000 tons/y) | 435 |

# *Thermodynamics Resource* is divided into gas-phase data and models of condensed-phase systems

- **Gas phase (Sandia)**
  - Data derived from *ab initio* quantum chemistry methods
  - Small molecules (typically < 20 atoms) expected to form at high T
- **Condensed phase (ORNL)**
  - Data derived by modeling using phase diagrams and critical assessments
  - Complex oxide glasses/liquids
  - Stoichiometric compounds
  - Models predict phase equilibria/activities
- **Both databases are continually updated and expanded**



# Project Tasks / Participants

**Tasks:**

1. **Thermodynamic modeling of condensed-phase systems**
   - Ted Besmann, ORNL
   - Nagraj Kulkarni, ORNL
2. **Prediction of high-temperature thermochemistry of gas-phase systems**
   - Mark Allendorf, SNL
   - Ida Beck Nielsen, SNL
   - Andrew Skulan (new postdoc), SNL
   - Carl Melius, LLNL
   - Beth Opila, Nate Jacobson, NASA/GRC
3. **Web site development**
   - Mark Allendorf, SNL
   - Michelle Medlin, SNL
   - Bill Dissly, SNL

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**Advisory committee**

- Dr. Usman Ghani, Air Liquide*
- Dr. Sandy Sharp, MeadWestvaco Corp.*
- Dr. David Russo, Atofina
- Dr. Randy John, Shell Oil
- Dr. John Connors, PPG Industries
- Dr. David Strickler, Pilkington-LOF
- Dr. Amul Gupta, Monafrax
- Dr. Dilip Patel, RHI Refractories
- Dr. Angel Sanjurjo, SRI International
- Dr. Ellen Meeks, Reaction Design

*** New member**

# Program plan/ Milestone status

**Milestone Plan**

- **Year 2**
  - **Make decision on ability to build comprehensive condensed-phase thermochemical model Decision to proceed; model successfully demonstrated**
  - **Develop, validate subcomponents for condensed-phase model Complete**
- **Year 3**
  - **Complete expansion of main-group gas-phase thermochemistry to include In, Sn, Sb ~80 new compounds of these elements added this year**
  - **Initiate model development for prediction of transition-metal thermochemistry Methods developed for Mn, Cr, and Fe; Method for Ti in progress**
  - **Models developed for Ca, Fe, Cr, Mn, Zr related condensed-phase oxide systems**
  - **Develop software to interconvert CHEMKIN and ChemSage/FACTSage thermodynamic fits in progress**
- **Year 4**
  - **Complete integrated web-based thermochemical information system**
  - **Complete theory for selected 2$^{nd}$-row transition metals (e.g., Y, Zr, Nb, Mo)**
  - **Complete experiments on Cr oxidation to test/validate theoretical methods**
  - **Integrate condensed-phase model subsystems into global models**
- **Year 5**
  - **Select best data from existing gas-phase data (> 3,000 species) and upload to web site (approximately 600 species transferred to date)**
  - **Continue to integrate/expand global condensed-phase models with critical systems**



# Task 1: Objectives

- **Develop practical models for calculating thermodynamic stabilities of components in complex oxides and glasses of value to design and use of refractories, glass manufacturing**
  - **Allow a large number of species/phases to be used**
  - **Make the model easy to understand and use**
  - **Base results on established phase-diagram data so it's reliable**
  - **Design for easy extension to other (T, $x_i$) regimes via interpolation or extrapolation**

***The modified associate species model is being used to predict thermochemistry for condensed-phase species in the database***



# Partial Experimental and Computed $Na_2O$-$B_2O_3$-$SiO_2$ Ternary Phase Diagrams Compare Well

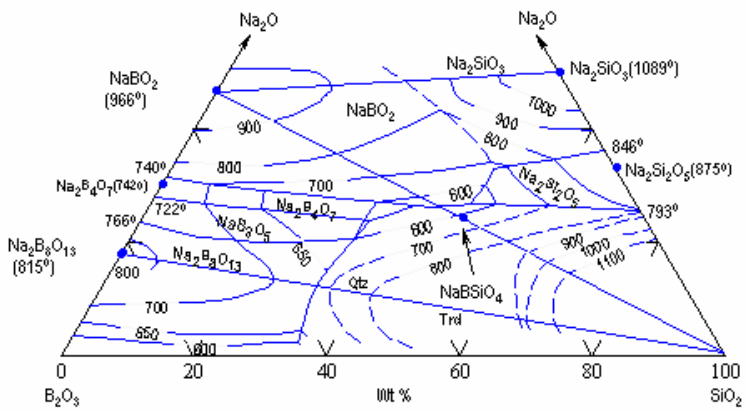
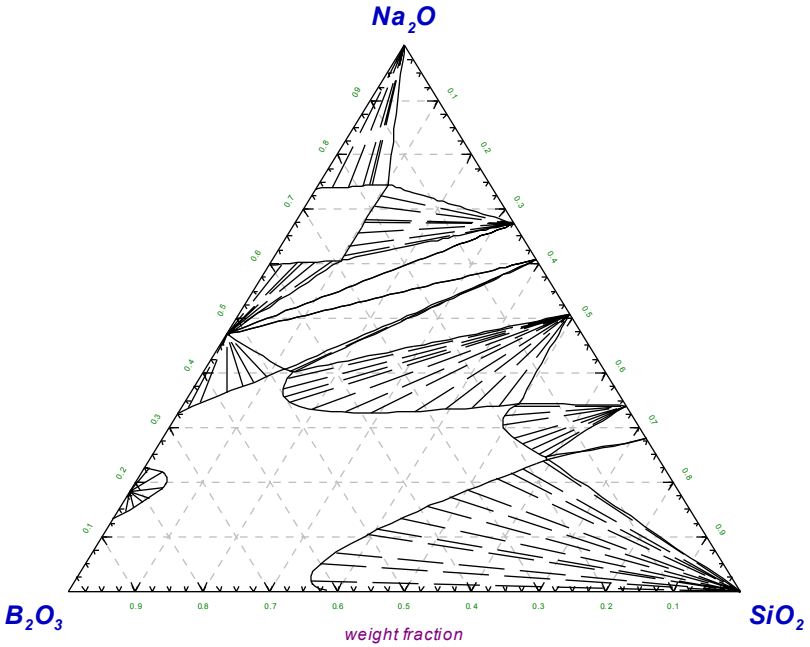



*Fig. 00515—G. W. Morey*



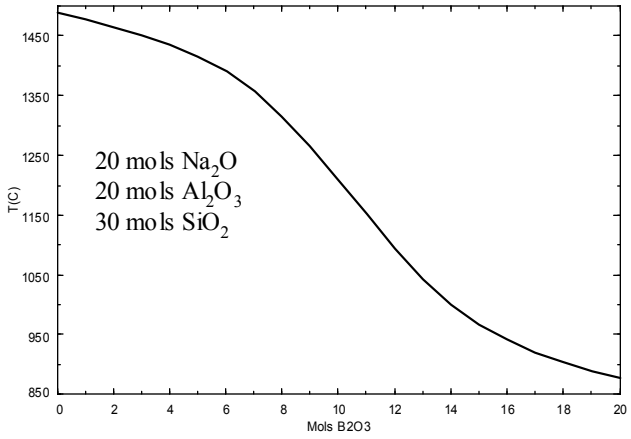

*Computed from associate species model - 800 °C*

# Boria Causes a Sharp Melting Point Depression Near Nepheline

***An additional soda-boria species was needed for the liquid model, $Na_3BO_3$:/2, and adjustments to the free energies of related species was necessary to obtain good agreement with experiment***

| $Na_2O$ (Mol %) | $Al_2O_3$ (Mol %) | $B_2O_3$ (Mol %) | $SiO_2$ (Mol %) | Exptl. $T_L$(°C) | Calc. $T_L$(°C) |
|---|---|---|---|---|---|
| 25 | 25 | 0 | 50 | 1510 | 1527 |
| 16.67 | 16.67 | 0 | 66.67 | 1124 | 1096 |
| 12.5 | 12.5 | 0 | 75 | 1085 | 1117 |
| 20 | 20 | 20 | 40 | 875 | 874 |

*Liquidus Variability with $B_2O_3$ Content*



# Calcia-Containing Systems Were Difficult to Model, But Resulting Models Are Accurate

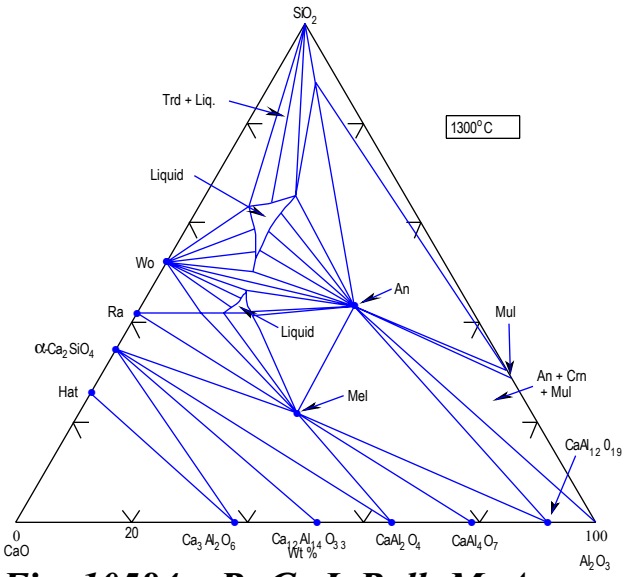
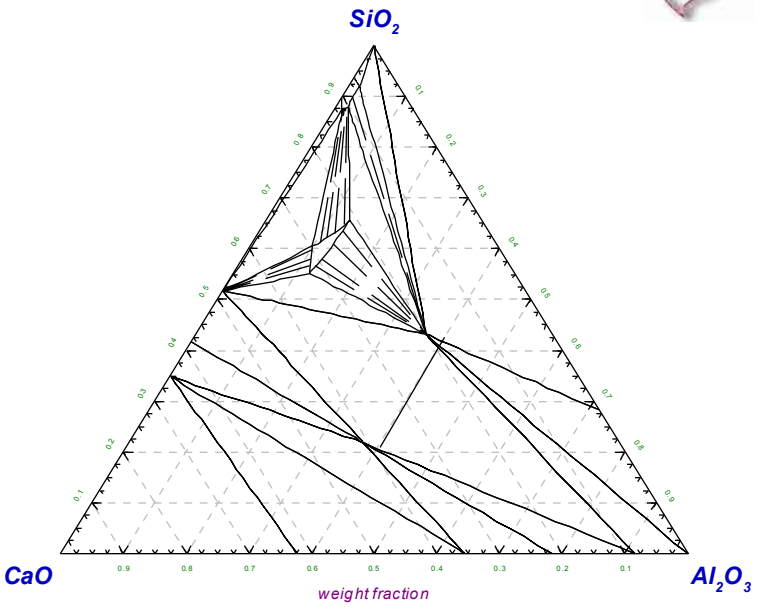



*Fig. 10584—R. G. J. Ball, M. A. Mignanelli, T. I. Barry, and J. A. Gisby - 1300 °C*




*Computed from associate species model - 1300 °C*

*Associates needed for the liquid/glass include: $Ca_2O_2$, $Ca_3Al_2O_6$:2/5, $Ca_2Al_2O_5$:/2, $CaAl_2O_4$:2/3, $CaAl_4O_7$:2/3, $Ca_3SiO_5$:/2, $Ca_3Si_2O_7$:2/5, $CaSiO_3$, $Ca_9Al_{10}SiO_{26}$:/10, $CaAl_2SiO_6$:/2, $Ca_3Al_2Si_3O_{12}$:/4 $CaAl_2Si_2O_8$:2/5, $Ca_2Al_2Si_6O_{17}$:/5*

# Summary - Task 1

- We have developed a refined, highly accurate base model for glass systems (Na-Ca-Al-B-Si-O) that agrees well with published phase diagrams.
- The modeling has been extended in to include subsystems with Fe, Cr, Mn, and Zr.
- The base glass and subsystems are being uploaded to the website

# Task 2: To calculate gas-phase thermodynamic data several pieces of information are required

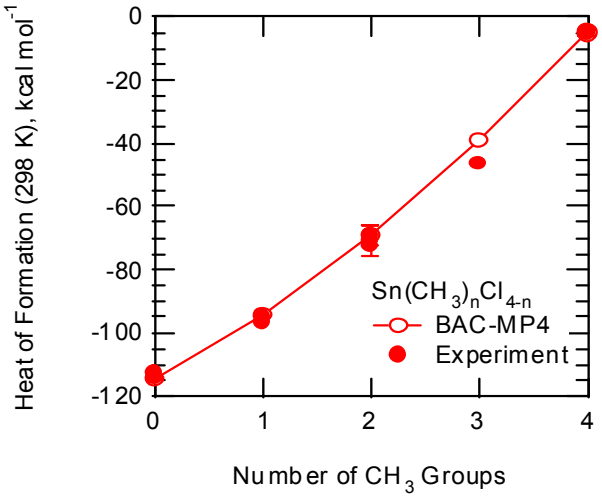
| Quantity | Required Inputs | Level of Calculation |
|---|---|---|
| Heat of formation | • Electronic energy with electron correlation<br>• Atomic heats of formation (from experiment) | • High<br>• Electron correlation required:<br>* Perturbation theory<br>* Coupled Cluster theory<br>* Configuration Interaction |
| Heat capacity | • Moments of inertia (molecular structure)<br>• Vibrational frequencies<br>• Barriers for internal rotation | • Low<br>• Electron correlation optional (HF, DFT, MP2) |
| Enthalpy, Entropy | Heat capacity | Statistical mechanics |

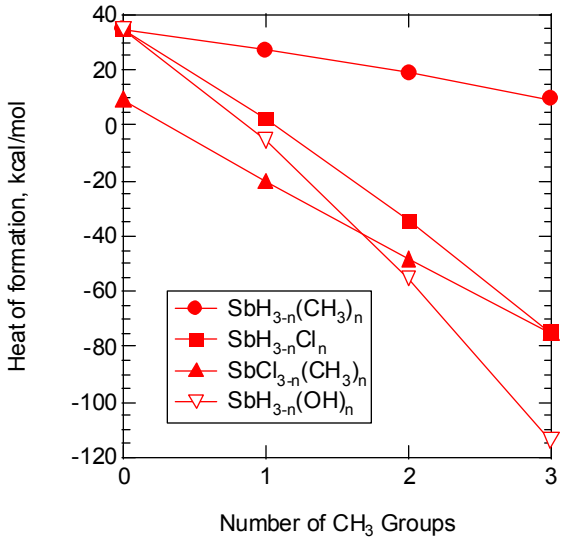
# We use the *Bond Additivity Correction* (*BAC*) suite of methods to predict molecular thermochemistry

- **BAC-MP4**
  - Original BAC method developed in 1980s for main-group compounds
  - Designed to be computationally practical
  - Recently modified to handle 4$^{th}$-row main group (In, Sn, Sb)
- **New class of BAC methods:** ***fewer parameters, greater accuracy***
  - **BAC-G2** ***High accuracy, broader applicability***
  - **BAC-MP2** } ***Useful for large molecules***
  - **BAC-DFT** }
  - **BAC-Coupled Cluster** ***Currently under development***
    - high accuracy
    - useful for highly unsaturated systems
    - "multireference" cases (e.g., diatomics, oxides, transition-metal compounds)
    - determination of reference thermo
- **Statistical mechanics routines to convert *ab initio* results to useful thermochemistry**
  - Scaled vibrational frequencies
  - Hindered rotor corrections

# The BAC-MP4 method is now upgraded to handle 4th-row main-group compounds (In, Sn, and Sb)

- Elements In, Sn, and Sb are not included in our original theory approach
- Relativistic effects are important for compounds of these heavy elements
- ➔ Uses relativistic effective core potential (ECP) to model the non-valence electrons:
  - $1s^2 2s^2 2p^6 3s^2 3p^6$ in core
  - $3d^{10} 4s^2 4p^n$ in valence
- Data obtained for tin and antimony compounds with these ligands:
  - H, $C_nH_{2n+1}$ (n=1-4), OH, Cl
  - Tin predictions agree well w/ available data (captures observed trends)
  - Antimony predictions are consistent with other main-group trends



# BAC-CCSD(T) results for compounds of heavy elements are in good agreement with the (limited) data

- **BAC parameters obtained by optimizing fit for a 70-molecule set (elements H, C, O, Cl, Ti, Sn)**
- **Heats of formation for tin compounds**
  - **Best available experimental data**
  - **Hi-level theory**
    - **CCSD(T)/triple- and quadruple-zeta correlation-consistent basis sets**
    - **Large-core pseudopotential**
    - **Isogyric reactions**
    - **Extrapolation to infinite basis set**
- **Titanium halides and small oxides**
  - **Experimental data available for all compounds examined**

| Compound | $\Delta H^\circ_f$ (kcal/mol) | Error* |
|---|---|---|
| SnO | 3.4 | -1.8** |
| $SnO_2$ | 10.1 | 0.7† |
| $H_2SnO$ | 33.6 | 1.3† |
| $H_3SnOH$ | -23.6 | -0.4† |
| $SnCl_2$ | -47.9 | 0.6** |
| $SnCl_4$ | -115.1 | -0.8** |
| $SnH_4$ | 36.3 | 0.3** |

| Compound | $\Delta H^\circ_f$ (kcal/mol) | Error* |
|---|---|---|
| TiCl | 47.2 | 1.9** |
| $TiCl_2$ | -47.3 | -0.3** |
| $TiCl_3$ | -120.7 | -1.9** |
| $TiCl_4$ | -182.2 | 0.2** |
| TiO | 12.2 | -0.8** |
| $TiO_2$ | -72.3 | 0.7** |

***Estimate (kcal/mol) from best available experiment (**) or theory (†)**

# We are developing methods to treat gas-phase compounds of Cr, Mn, Fe,

- **Cr, Mn, and Fe are common components of both refractories and metal alloys**
- **Corrosion by halides occurs in a number of industrial environments**
- **Thermodynamic data are available in the literature to test and establish methods**
- **Theory is mostly in agreement with the experimental values**
- **Oxides and hydroxides will be treated next**

| Compound | Theory | Experiment |
|---|---|---|
| MnF | –17.8 | –5.2 |
| $MnF_2$ | –130.1 | N/A |
| MnCl | 17.6 | 15.8± 1.6 |
| $MnCl_2$ | –62.6 | –62.6 ± 1 |

| Compound | Theory | Experiment |
|---|---|---|
| FeF | 11.9 | 11.40 ±4.78 |
| $FeF_2$ | –104.7 | –93.10 ±3.39 |
| FeCl | 49.8 | 49.5 ±1.6 |
| $FeCl_2$ | –33.4 | –33.7 ±0.5 |

| | Theory | Experiment |
|---|---|---|
| CrF | –5.2 | 4.57 ± 2.41 |
| $CrF_2$ | –105.3 | –103.23 ± 2.96 |
| CrCl | 30.9 | 31.05±0.65 |
| $CrCl_2$ | –36.9 | –28.11 ± 0.41 |

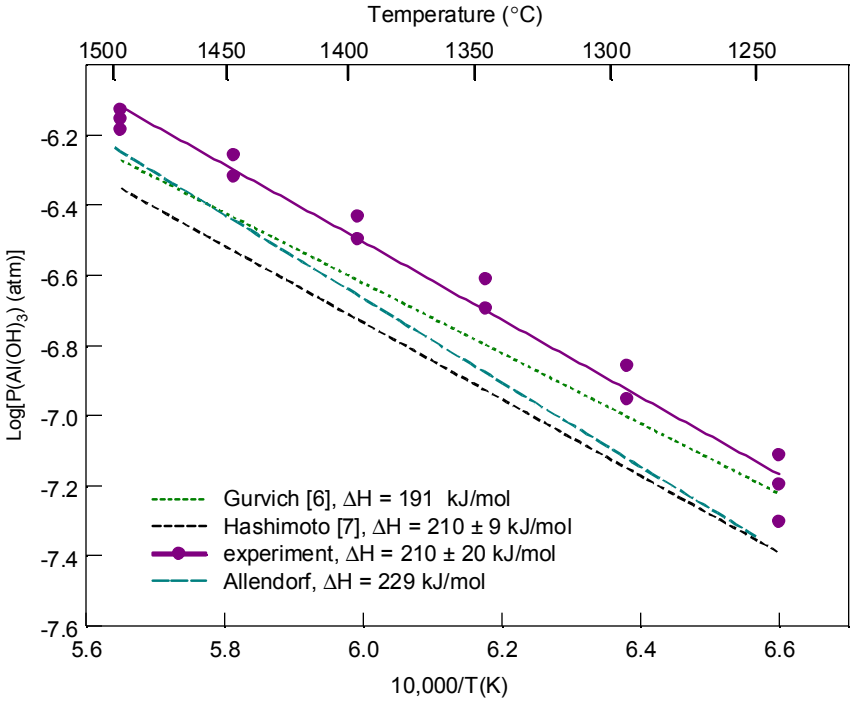
# New experimental results continue to validate BAC-MP4 predictions for high-temperature species

Volatilization of alumina by steam:

$Al_2O_3(cr) + H_2O(g) = Al(OH)_3(g)$

Data fit using BAC-MP4 prediction for $Al(OH)_3$ heat of formation

Allendorf et al, *J. Phys. Chem.A*, 2002



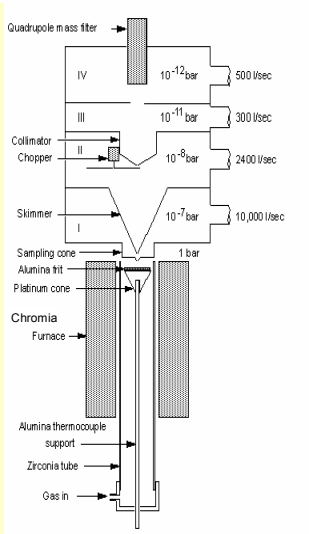

**Comparison of experiment with theory for $Al(OH)_3$ as a function of temperature**

**Transpiration/mass spectrometry experiments**
**Data from Jacobson et al.**
**NASA/Lewis Research Center, 2003**

# Volatile chromium species play a key role in the high-temperature performance of Cr-containing materials

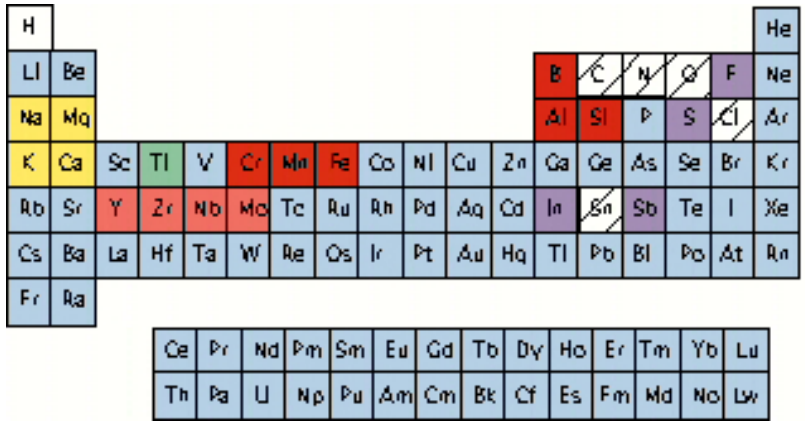
- $Cr_2O_3$ is volatile in high-temperature water vapor environments:

  $1/2\ Cr_2O_3(s) + H_2O(g) + 3/4\ O_2(g) \rightarrow CrO_2(OH)_2(g)$
- Volatility leads to reduced lifetime for Cr-base materials and contamination of system with $Cr_2O_3$. Applications include:
  - Chrome-containing refractories
  - Chrome-plated tubing
  - Chromium-containing alloys
- Strategy:
  - Measure volatility using transpiration technique
  - Use Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) to quantify concentration of Cr-containing species
  - Determine enthalpy and entropy of volatilization reaction




*These experiments will lead to thermodynamic data that can be compared with theory to validate computational methods for transition metals*

# Status of gas-phase database - Year 3 activities




| | | | |
|---|---|---|---|
| H | Complete | F | Data available but not uploaded |
| C | Partially uploaded dataset | Sn | New method and data |
| B | Newly added data | In | Method under development |
| Na | Data available elsewhere | Tl | New elements for PY4 |

- **Data now available**
  - **> 850 compounds on line**
  - **60 new Sn-H-C-Cl compounds**
  - **> 400 C-H-O compounds**
  - **66 Al-H-C-N-O-F-Cl compounds**
  - **> 200 Si-H-C-N-O-F-Cl compounds**
  - **47 Si-B-H-Cl compounds**
  - **Ti, Cr, Mn, Fe hydrides, halides, fluorides, hydroxides (projected 9/30)**
- **Method development**
  - **40% staff member and 50% postdoc dedicated to method development**
  - **New coupled-cluster BAC method for Ti, Cr, Mn, Fe compounds**
- **Database development**
  - **Expansion of 1st-row transition metals**
  - **Extension to 2nd row in PY4**
  - **Additional main-group compounds (C7 – C10; more tin data)**

# Task 3: Database/Website development - Year 3 activities

**Site is open to the public! Data are available at NO CHARGE!**

**www.ca.sandia.gov/HiTempThermo/index.html**

**Condensed-phase data:**

- **Extensive data set for important industrial materials systems:**
  - **Refined $Na_2O$-CaO-$Al_2O_3$-$B_2O_3$-$SiO_2$ system for modeling base glass systems uploaded.**
  - **The modeling has been extended to include subsystems with Fe, Cr, Mn, and Zr and partial systems uploaded.**

**Gas-phase data:**

- **New gas-phase thermochemistry**
  - **> 400 C-H-O species relevant to natural-gas combustion**
  - **120 B-H-C-N-O-Si-Cl**
  - **66 Al-C-N-O-F-Cl species**
  - **> 200 Si-H-C-N-O-F-Cl (new)**
  - **> 60 Sn-H-C-Cl compounds (new)**
  - **Sb-H-C-Cl data (new)**
  - **Mn, Cr, Fe data (new)**

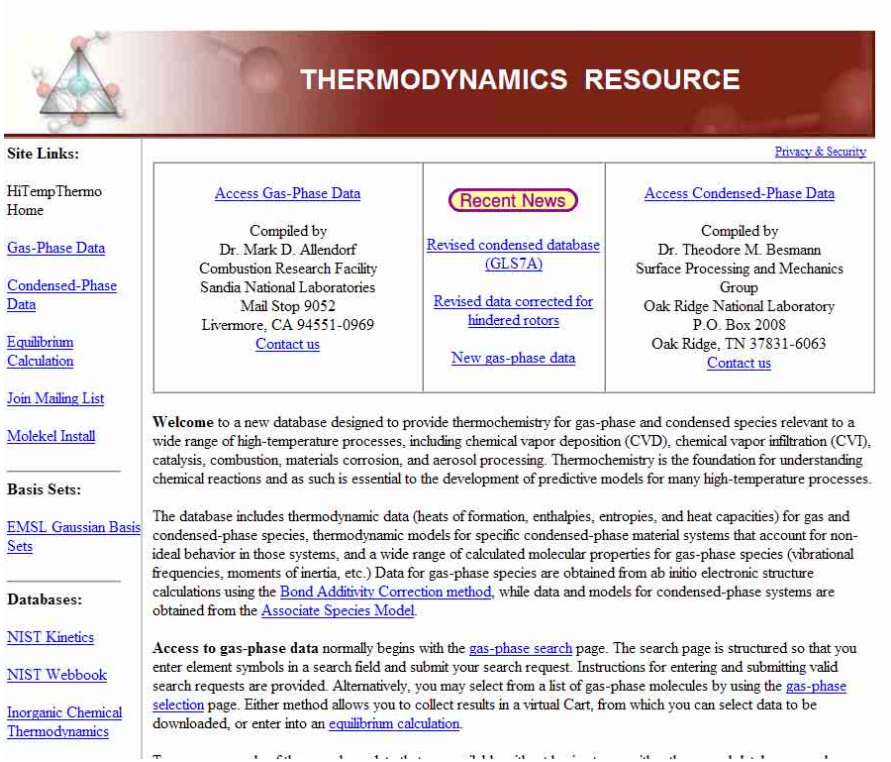
*Our data are well documented with a clear pedigree, unlike most commercial (encrypted) databases*



# Site enhancements and management

**Numerous features and upgrades to site structure, including:**

- **"Recent News" page**
- **Archived earlier versions of data**
  - **Allows comparisons with previous versions to assess the effects of changes**
- **On-line equilibrium calculator**
  - **User can access data and perform an equilibrium calculation with selected species, T, P**
  - **Uses Sandia/Reaction Design EQUIL/CHEMKIN software**
- **Improved search engine allows much greater flexibility to select species subsets**



# Feedback from users provides useful insight into improvements and needed data

- Industry advisory group
  - Two new members covering pulp/paper and chemicals industry
- On-line user community
  - Users may “subscribe” - 78 to date
  - Provides ability to keep community informed of developments and changes in the database
  - User-provided suggestions are being incorporated into the site
  - Users also lead us to other resources (data, software, etc.)
  - ~ 2,500 hits/year in first two years!

# Getting the word out

- **Brochure designed with logo for site**
  - **Mailed to > 1,500 individuals**
  - **Distributed at major technical conferences**
- **Publications and presentations**
  - **Presentations at technical conferences:**
    - **American Ceramic Society Spring 2004 meeting**
    - **American Chemical Society Spring 2004 meeting**
    - **American Institute of Chemical Engineers Fall 2003 meeting**
- **Links to other web sites:**
  - **Link to DOE/OS Collaboratory for Multi-scale Chemical Science**
  - **Materials Research Society**
  - **American Ceramic Society**
  - **The Electrochemical Society**
  - **Reaction Design Inc. (supplier of software to the chemicals and combustion industries)**

# Plans for FY05

- Task 1
  - Expand condensed-phase dataset for K, Mg, Cr, Ti, P oxides, and generate increasingly large global models.
- Task 2
  - Expand database of gas-phase transition-metal thermo for first-row compounds (primarily Ti, Cr, Mn, Fe)
  - Develop methods to predict data for Zr, Y, Nb, Mo ($2^{nd}$-row tran. metals)
- Task 3
  - Expand data relevant to combustion processes, esp. NOx-related and halogenated hydrocarbons
  - Complete software for CHEMKIN-FactSage format interconversion
  - Provide user tutorials and examples for on-line equilibrium calculator
  - Upload new condensed phase models to the website
  - Explore educational possibilities via interactions with universities